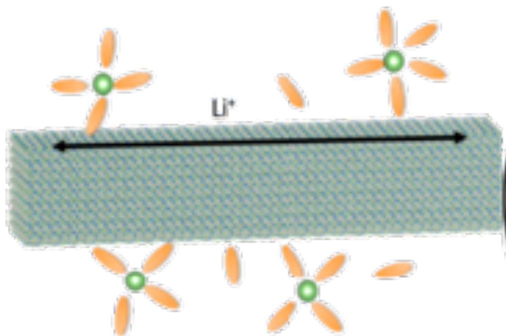
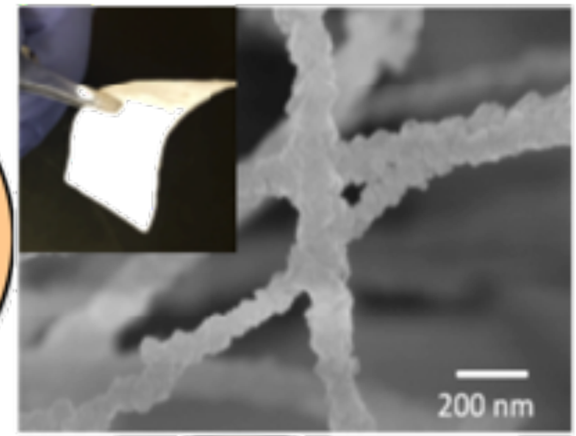
High Conductivity and Flexible Hybrid Solid State Electrolyte

Eric D. Wachsman, Liangbing Hu, Yifei Mo



MO (Computation):
- Mechanical flexibility;
- Ion transport on surface and interface;
- Li metal dendrite;
- Interface impedance.



WACHSMAN (Experiment):
- Nanofibers with optimized garnet composition, process and dimensions;
- FIB/SEM structures

Flexible, Solid State Hybrid Electrolyte

HU (Experiment):
- Hybrid electrolyte
- Li metal anode with hybrid electrolyte;
- Li-S cells with hybrid electrolyte.

Project ID: BAT322

Overview

Timeline

- Project Start: October 1, 2016
- Project End: September 30, 2019
- Percent Complete: 50%

Budget

- Total Project Funding: $1,388,889
  - DOE Share: $1,250,000
  - Cost Share: $138,889
- FY 2016 Funding received: $1,250,000

Barriers

- Solid state batteries are known for high bulk and interfacial impedance and are inherently rigid
- Organic electrolytes are less stable, flammable, have limited mechanical strength or ability to block dendrites
- A balance is needed that combines the advantages of both types of electrolytes to enable Li-metal batteries

Partners

- Longstanding collaboration with Prof. Venkataraman Thangadurai

Relevance

Objectives

- Develop high-conductivity (>0.5 mS/cm), flexible, low-interfacial impedance garnet-organic hybrid electrolytes based on garnet nanofibers.
- Demonstrate Li-S batteries with ~450 Wh/kg for 500 cycles

Impact

- A hybrid flexible solid electrolyte will enable high-energy density, safe Li metal batteries with 2-3X energy density that can still be processed within existing battery manufacturing infrastructure

Milestones and Approach

Approach

Use computational modeling and experiment to:

- Determine Li diffusion, Li dendrite protection, and mechanical properties of garnet, polymer electrolytes, and hybrid electrolytes
- Characterize electrochemical, mechanical, and thermal properties of hybrid electrolytes
- Optimize hybrid electrolyte and produce full cell Li-S battery delivering 450 Wh/kg for 500 cycles

		Year 1				Year 2				Year 3			
	Name(Task, Subtask, Milestone)	Q 1	Q 2	Q 3	Q 4	Q 5	Q 6	Q 7	Q 8	Q 9	Q 10	Q 11	Q 12
1	**Task 1: Develop computational models**												
2	**Task 2: Synthesize and characterize garnet nanofibers**												
3	**Task 3: Fabricate hybrid solid state electrolyte**												
4	**Task 4: Determine structure and properties of hybrid electrolyte**												
5	**Task 5: Li-hybrid electrolyte interface**												
6	**Task 6: Fabricate and test Li-S full cells**												

FY18Q1 Milestone: Fully characterize microstructures with FIB/SEM and AFM (**Completed**)

FY18Q2 Milestone: Characterize electrochemical, mechanical, & thermal properties of hybrid SSE (**Completed**)

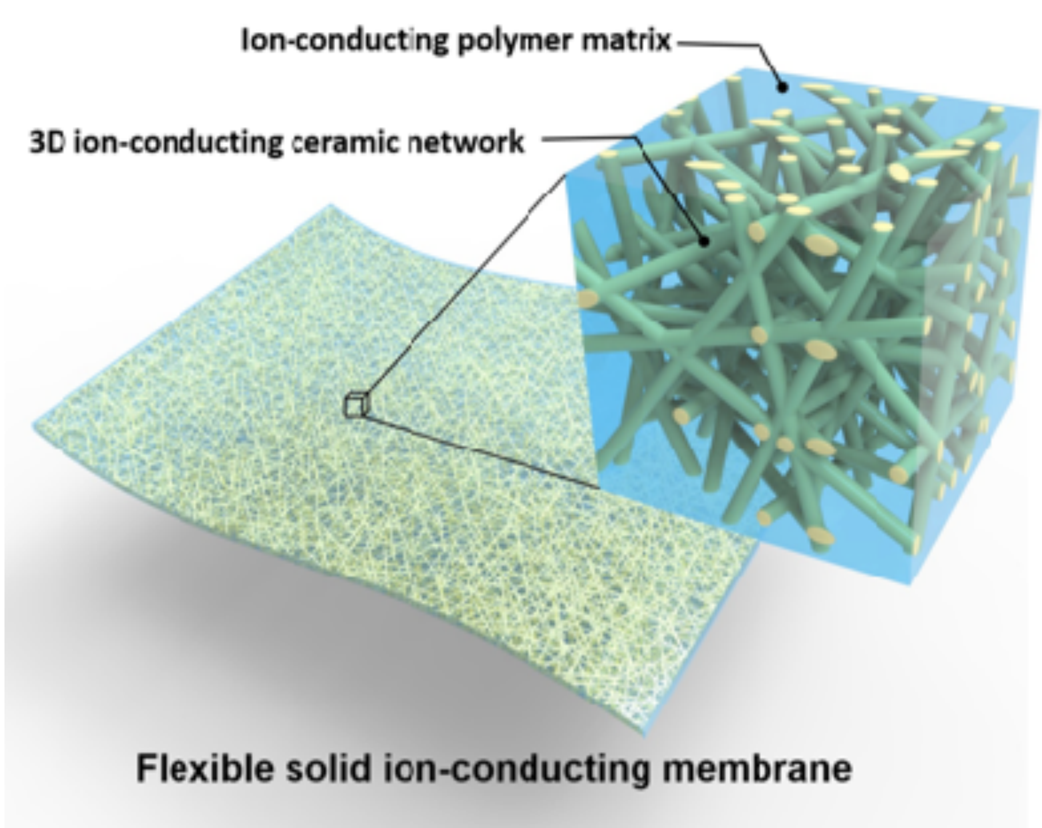
FY18Q3 Milestone: Fabricate 20 μm thick hybrid SSE and understand Li-interface (**Completed**)

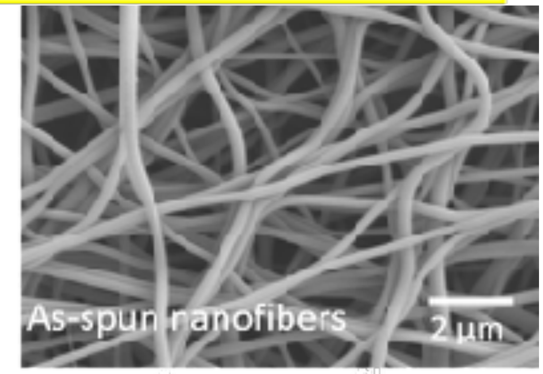
FY18Q4 Milestone: Understand Li stripping/plating in thin SSE at current density of 3 mA/cm^2

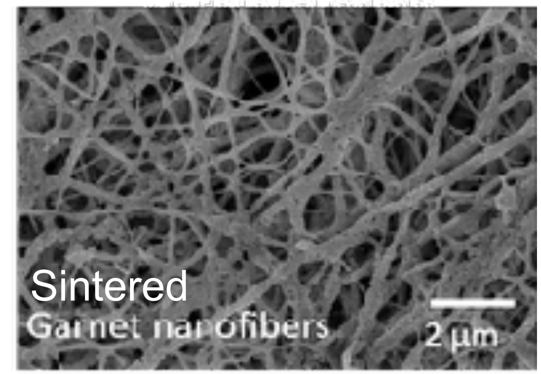
Developed Hybrid Garnet/Organic Cells from Electrospun Fibers

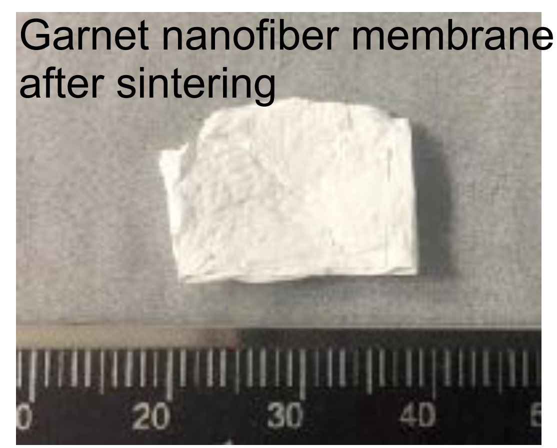
PNAS

Flexible, solid-state, ion-conducting membrane with 3D garnet nanofiber networks for lithium batteries



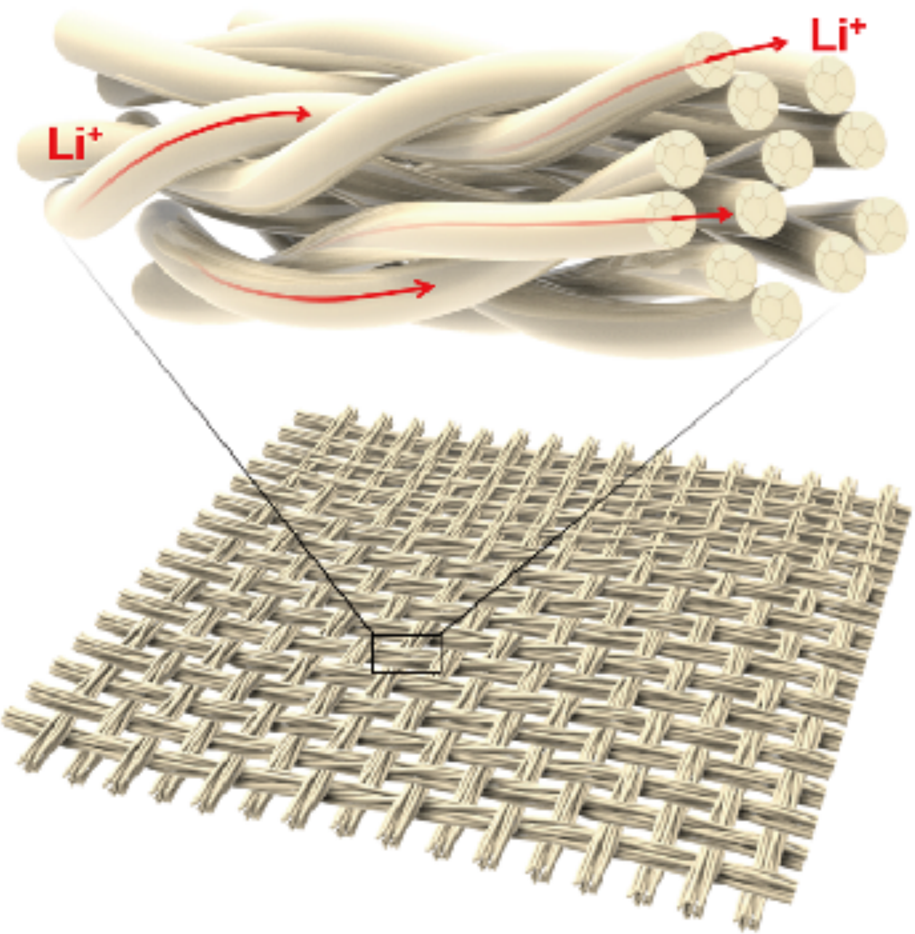


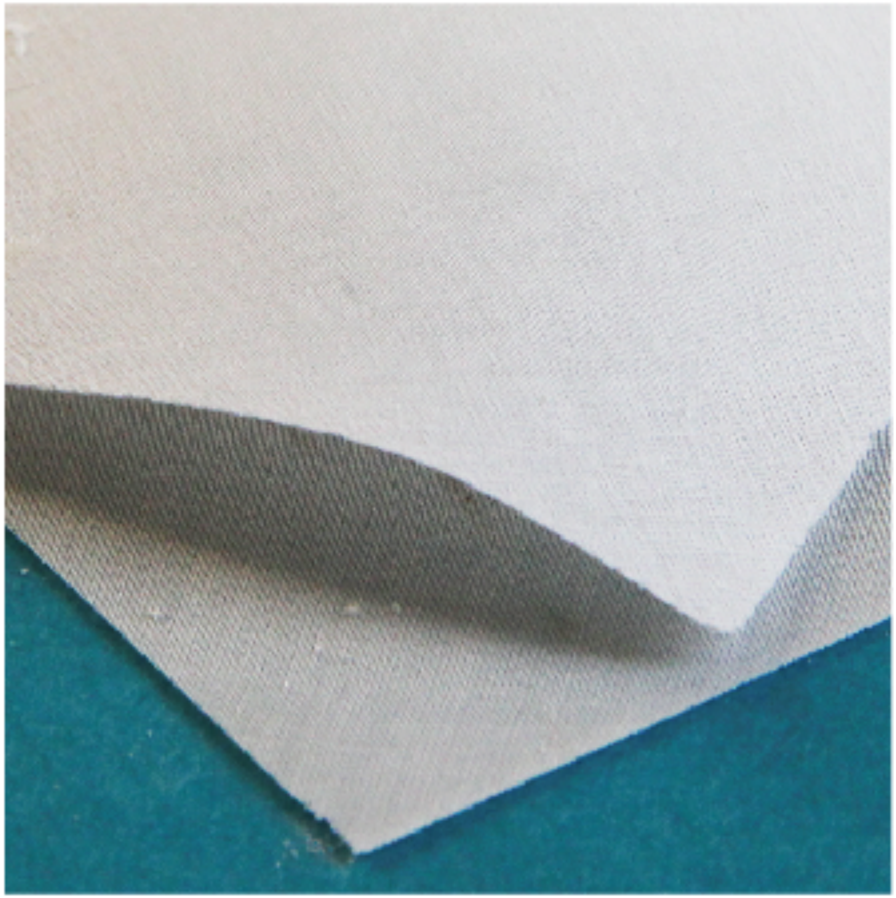




Developed Hybrid Garnet/Organic Cells from Templated Garnet

Design of fibrous garnet textile

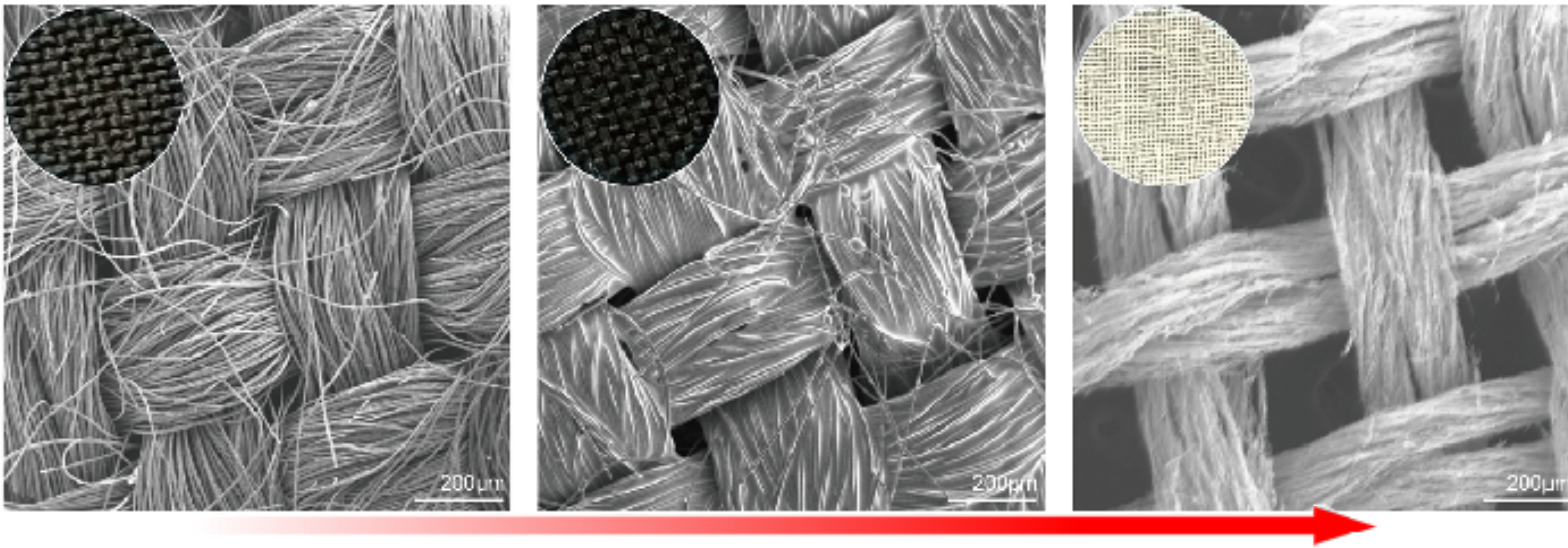




- Lithium ion conductive.
- Low gravimetric density.
- High surface area/volume ratio.
- Flexible.

Developed Hybrid Garnet/Organic Cells from Templated Garnet

Template replica fabrication process

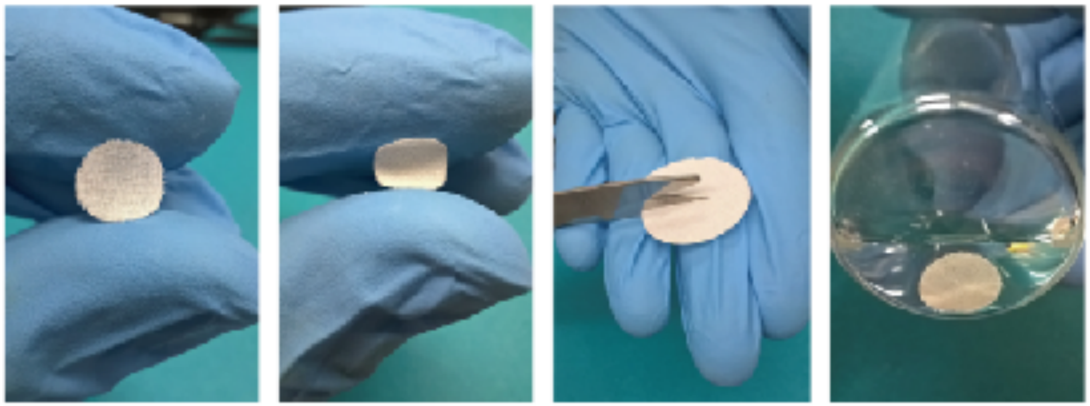


Textile template

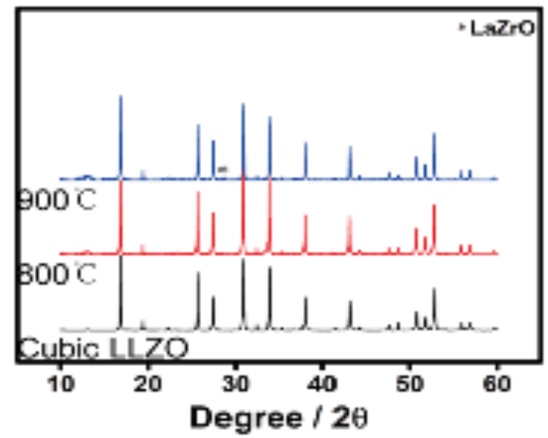
Precursor impregnated textile template

Garnet textile

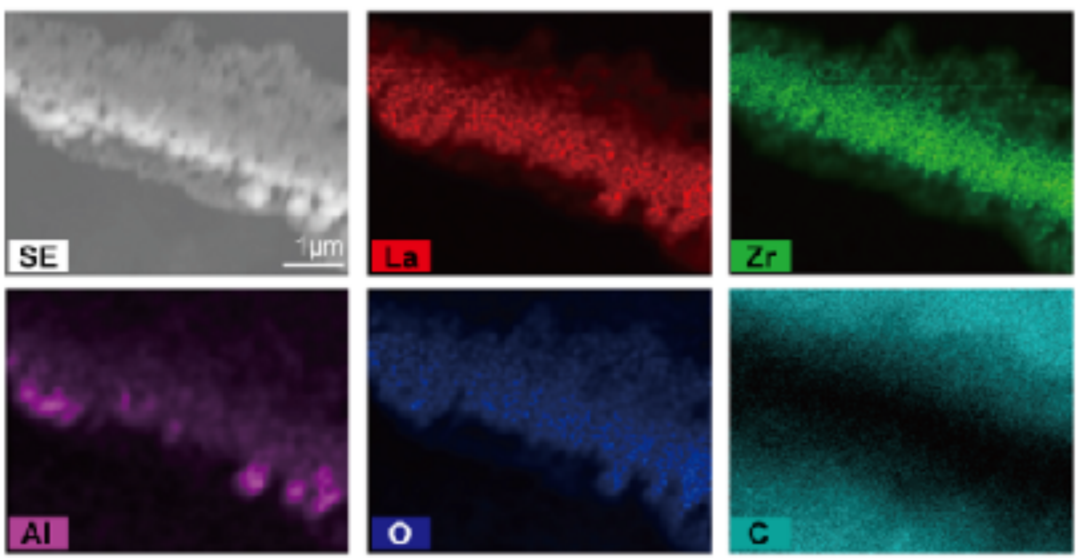
Developed Hybrid Garnet/Organic Cells from Templated Garnet



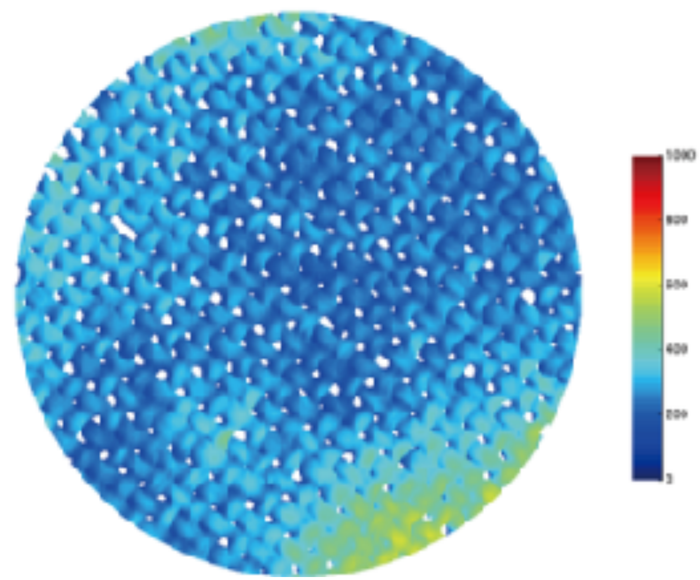
Flexibility and workability



Demonstrated Cubic phase



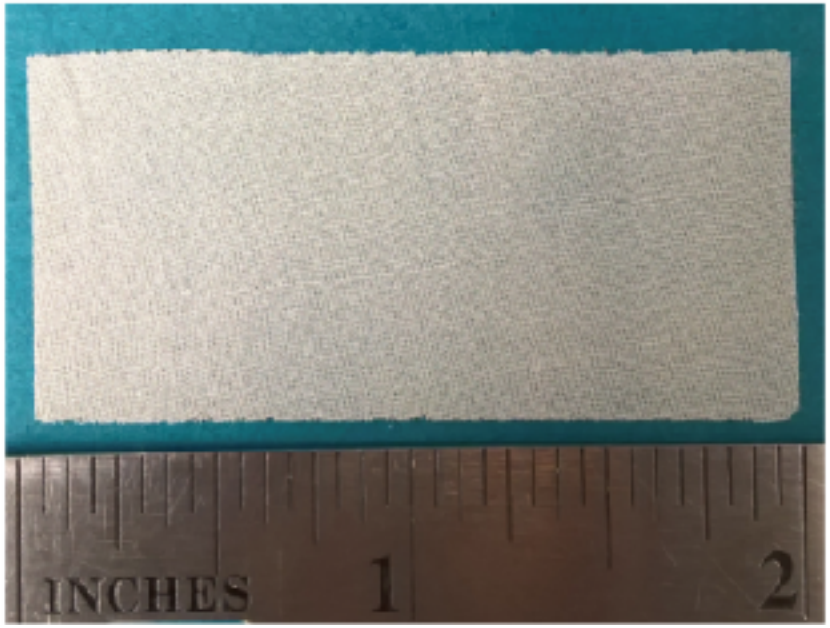
Elemental distribution demonstrating garnet composition



Demonstrated flatness

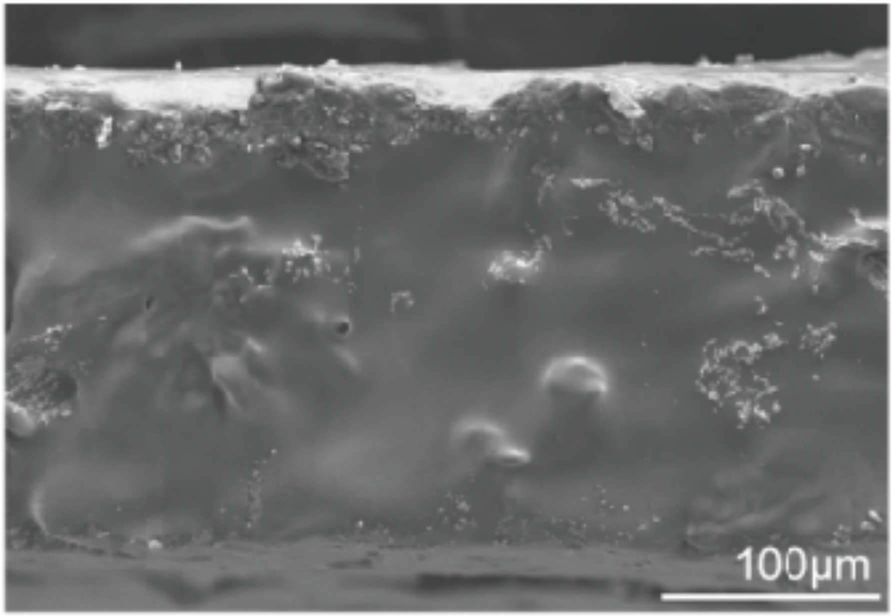
Developed Hybrid Garnet/Organic Cells from Templated Garnet

Simple, Rapid, Low-cost, Scalable fabrication of garnet textile



- Low gravimetric density.
- Flexible.

Garnet textile reinforced Hybrid Composite Polymer Electrolyte



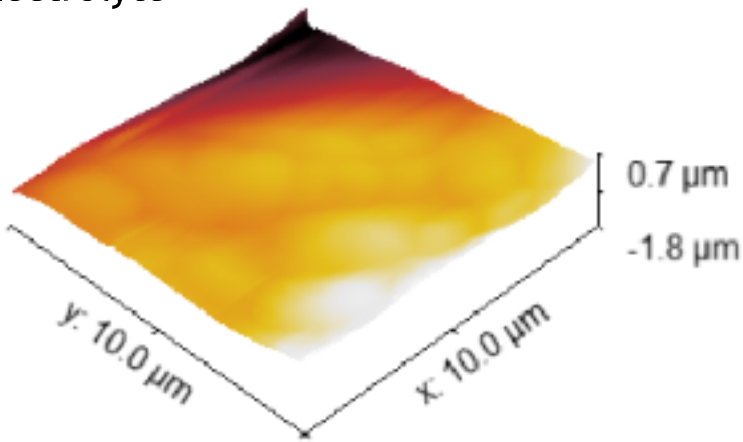
- Lithium ion conductive.
- Dense and free of pores.

FY17Q1 Milestone - Fabricate large area garnet fibers

FY17Q2 Milestone - Synthesize polymer electrolyte coated garnet fibers

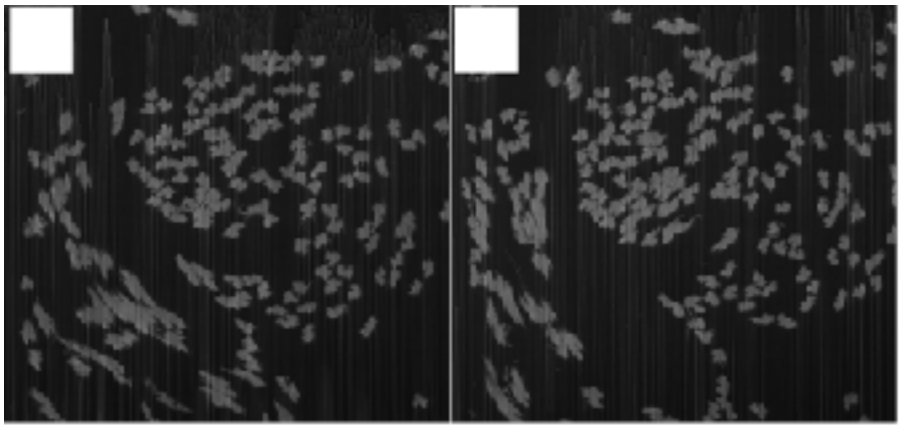
Microstructure and Surface Properties of Hybrid Electrolyte

AFM of the hybrid polymer/ garnet textile composite electrolyte



The polymer material was infiltrated to fully fill the open pores and cover the surface of the individual fibers within the textile structure. The surface roughness of the composite electrolyte was controlled with the value of less than 2 μm.

Focus ion beam analysis of the typical fiber bundle structure in garnet textile.



The ceramic particles of the fiber mat sample are visible in the front side of the region of interest.
The continuous ceramic fiber structure provides structure reinforcement and abundant fast Li-ion conductive path within the composite electrolyte.

FY18Q1 Milestone: Fully characterize microstructures with FIB/SEM and AFM (**Completed**)
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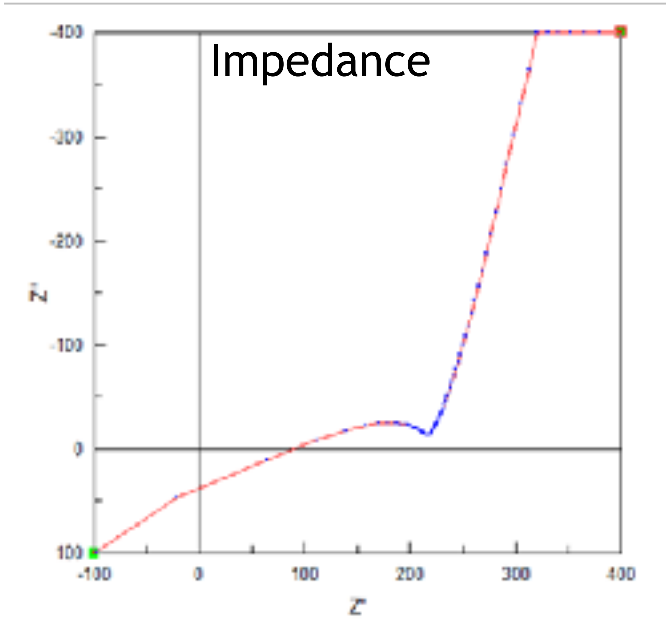
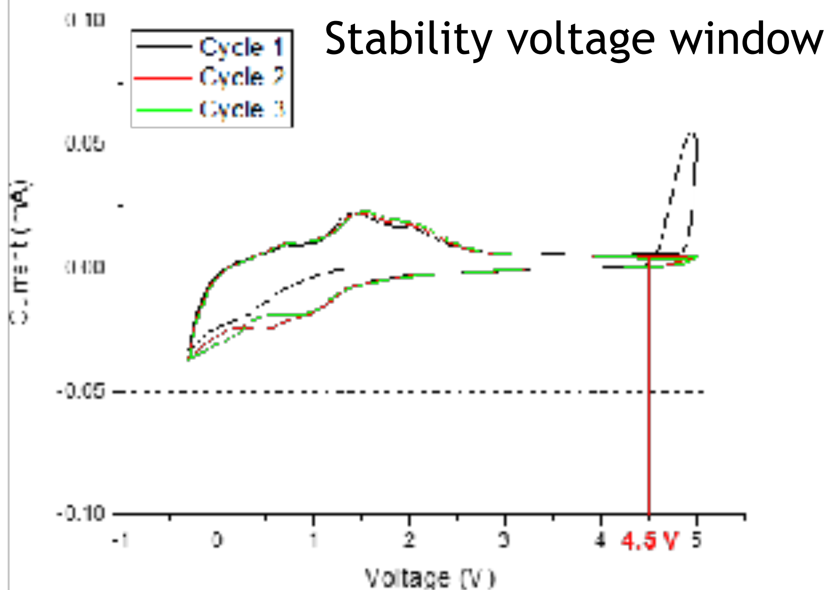
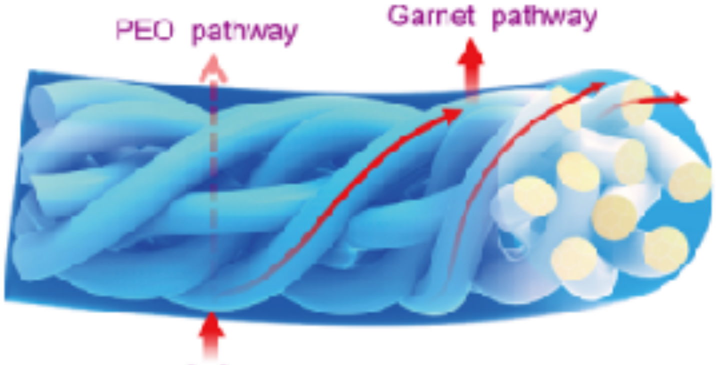
Electrochemical Properties of Hybrid Electrolyte

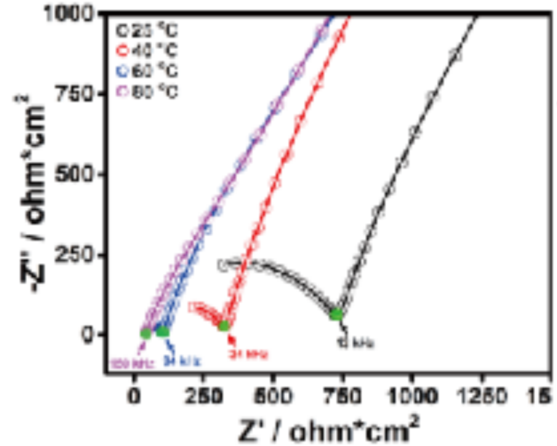


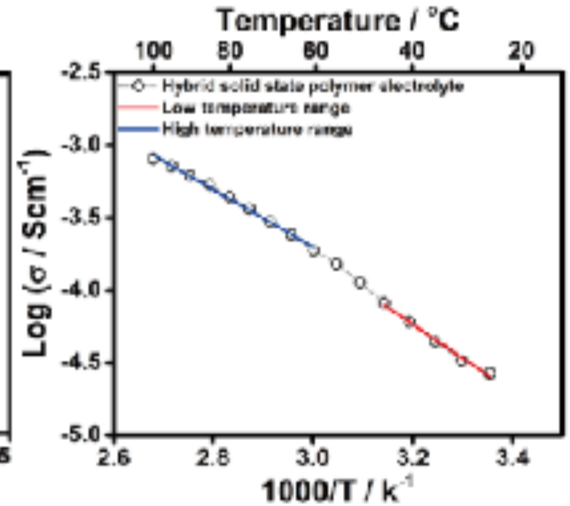


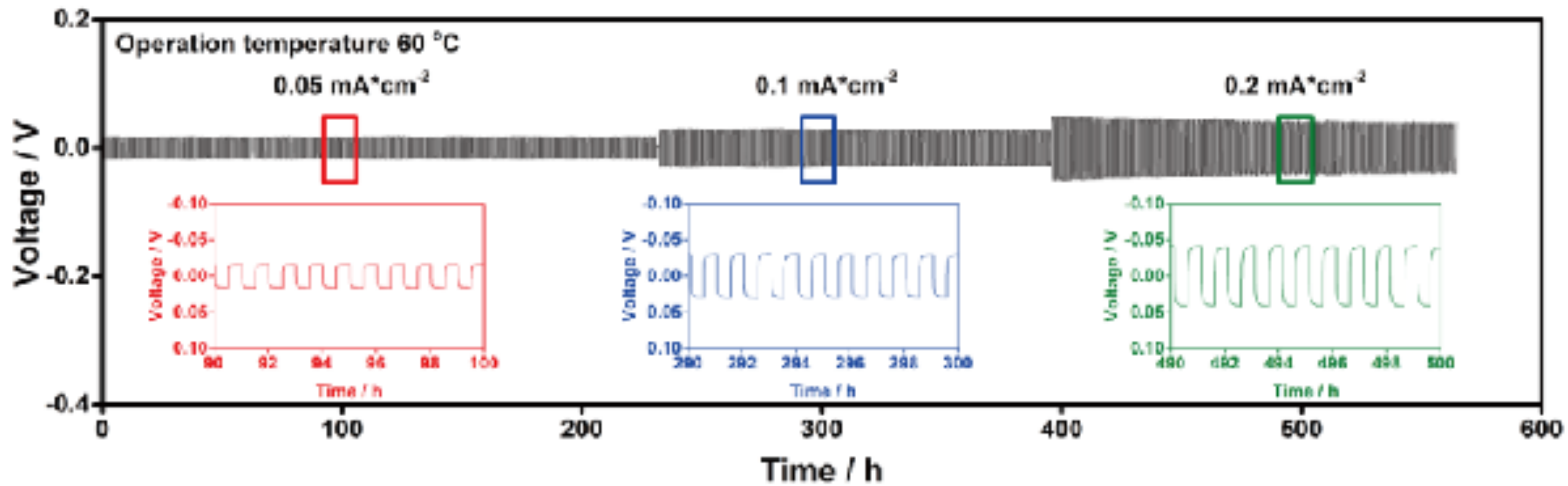
- The Li-ion conductivity of the hybrid solid-state electrolyte is 6.07×10^{-4} S/cm measured at room temperature.
- The electrochemical voltage window is stable up to 4.5V.

Electrochemical Properties of Hybrid Electrolyte



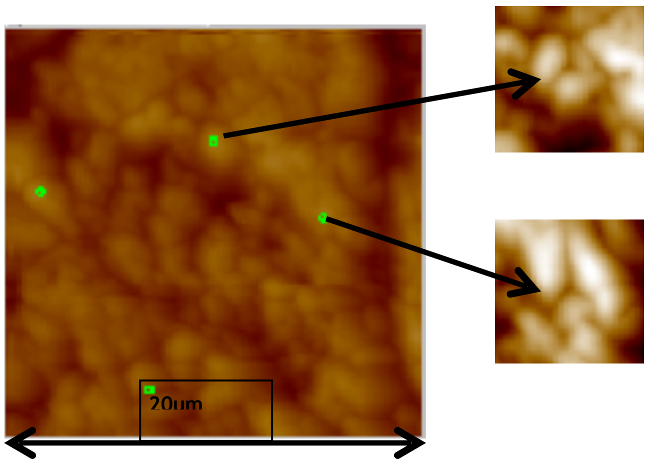


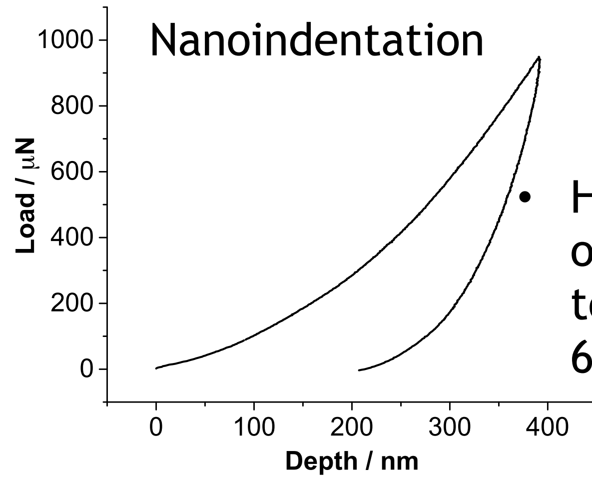




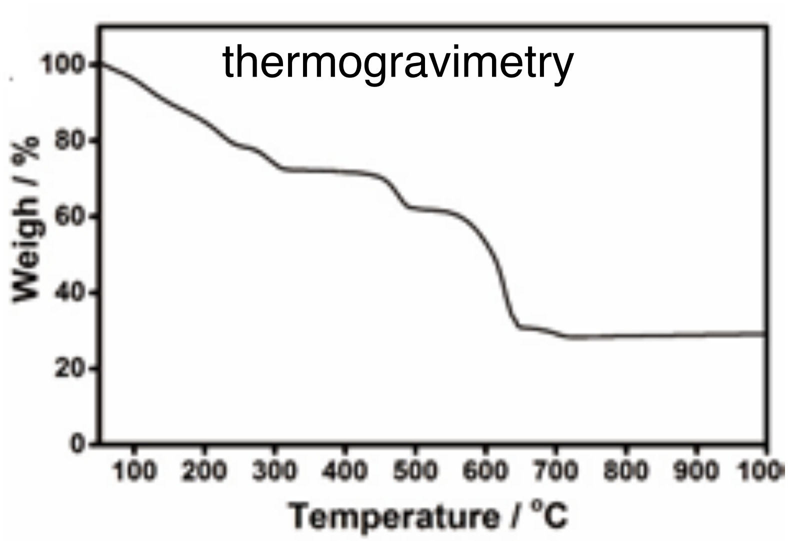
Stable cycling of polymer electrolyte coated garnet fibers

Mechanical and Thermal Properties





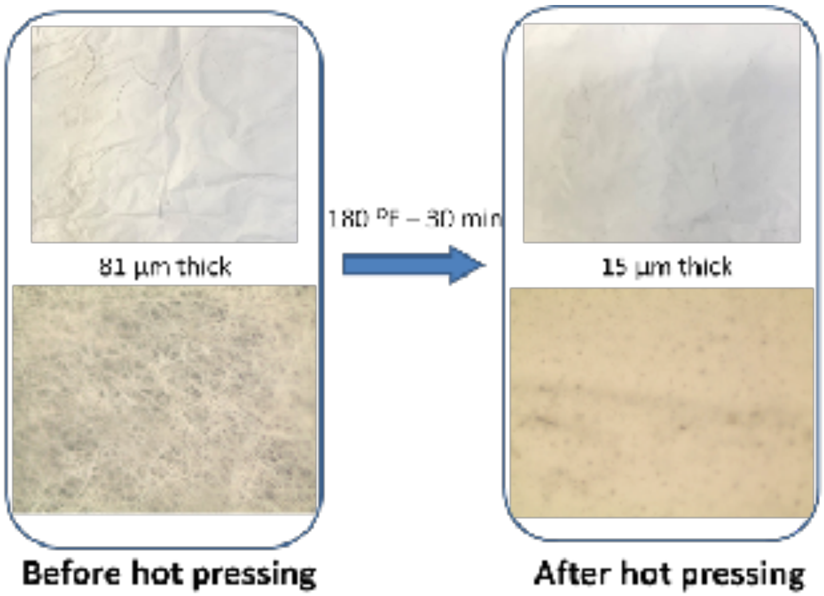
- Hardness and Young's modulus of garnet fiber was measured to be 0.28 ±0.04 Gpa and 6.3±0.5 Gpa, respectively.

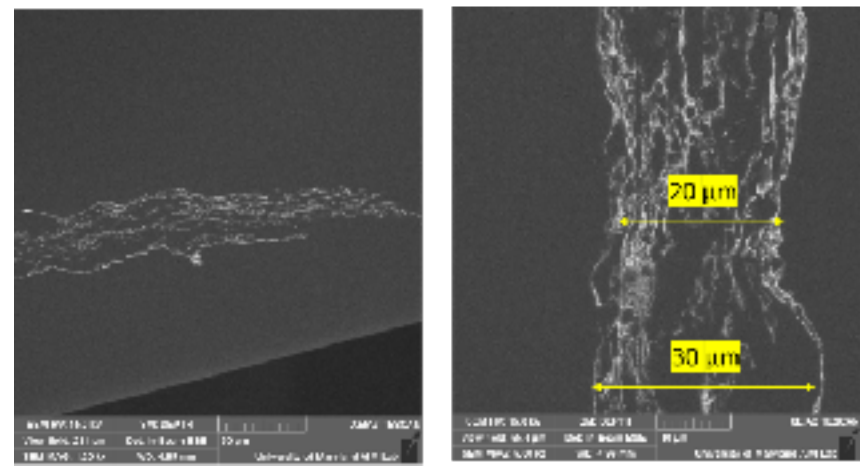


- The weight loss is caused by evaporation of the trapped solvent from room temperature to 300 °C. The hybrid electrolyte shows thermal stability up to 450 °C. After final decomposition at 600 °C, the garnet phase was the only component left.

FY18Q2 Milestone: Characterize electrochemical, mechanical, & thermal properties of hybrid SSE (**Completed**)

Thin HybridElectrolyte with Thickness of 20 μm





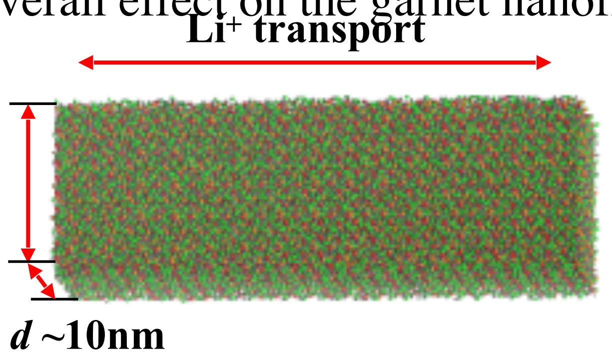
- PAN fiber mat by electrospinning was 81 μm thick on the left. To reduce the thickness and retain the fiber structure, hot press was applied and the final thickness of 15 μm was achieved.
- The thickness of the garnet framework is 20-30μm with a typical layer structure of the ceramic fiber phase.

FY18Q3 Milestone: Fabricate 20 μm thick hybrid SSE and understand Li-interface (**Completed**)

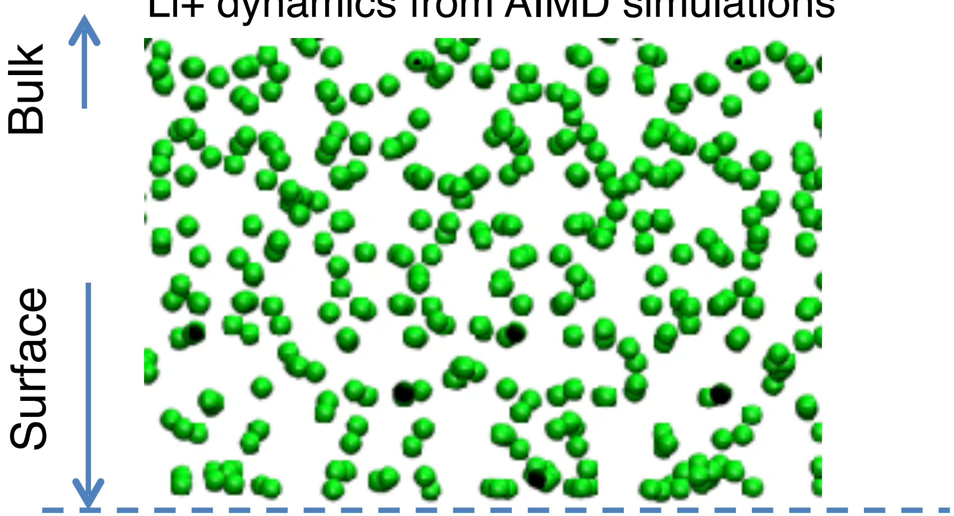
Understanding Garnet Nanofiber Li Diffusion: MD simulations

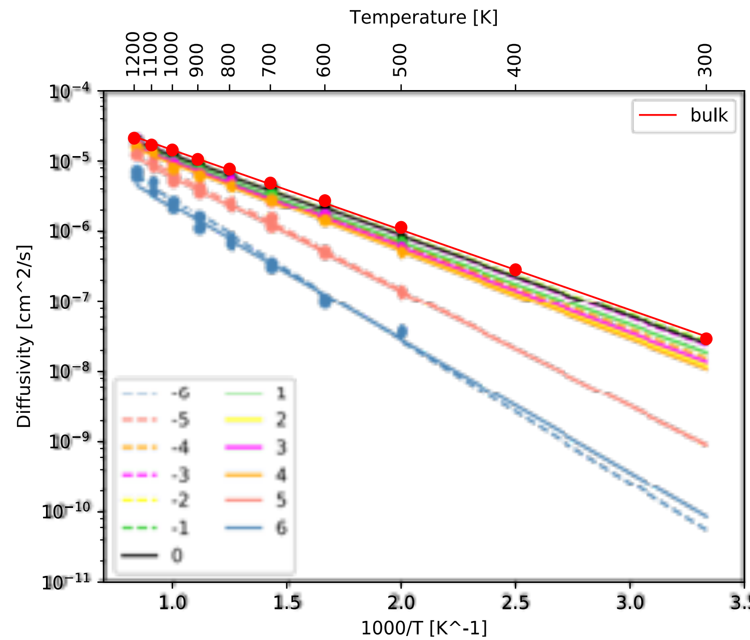
Li+ diffusion in garnet nanofiber is directly modeled using MD simulations.

- Li+ concerted migration is observed in the bulk of garnet phase.
- Li+ diffusion slows down near the surface region (<1nm) of garnet.
- The overall effect on the garnet nanofiber transport is small and negligible



Li+ dynamics from AIMD simulations





Li+ conductivity in different regions near the surface of nanofiber. Only out-most surface layers (<1nm) show decrease. The nanofiber diffusion is largely unaffected.

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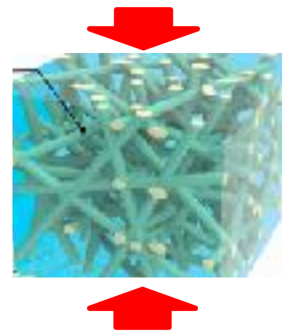
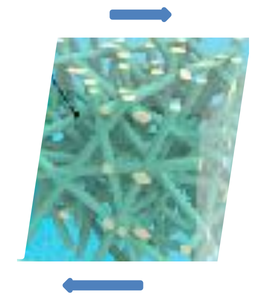
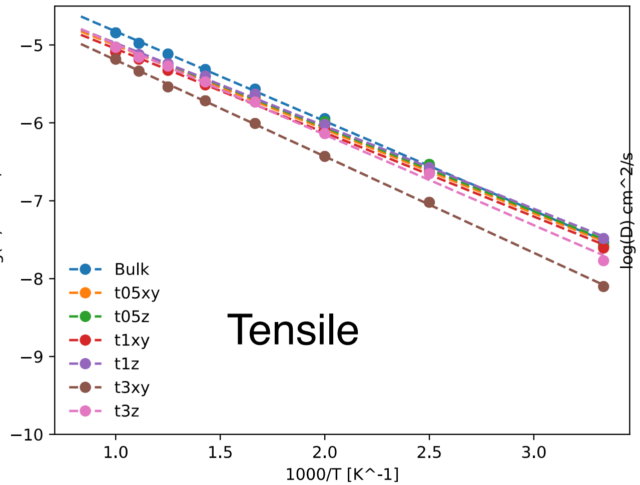
Mechanical Response of Li Diffusion in Garnet Nanofiber

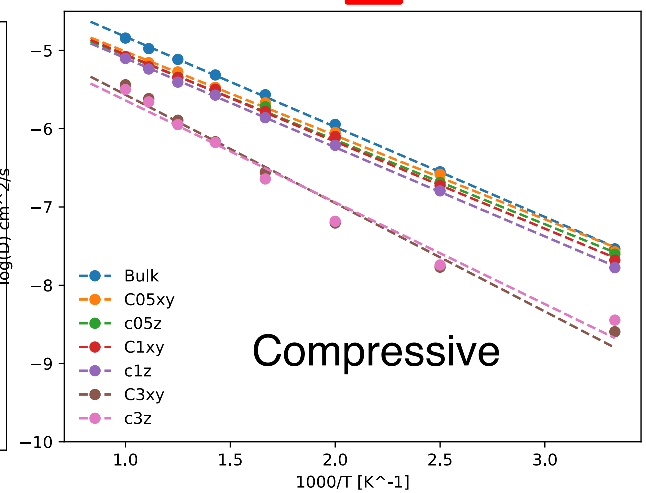
Li+ diffusion in garnet nanofiber under mechanical deformation is evaluated using MD simulations.

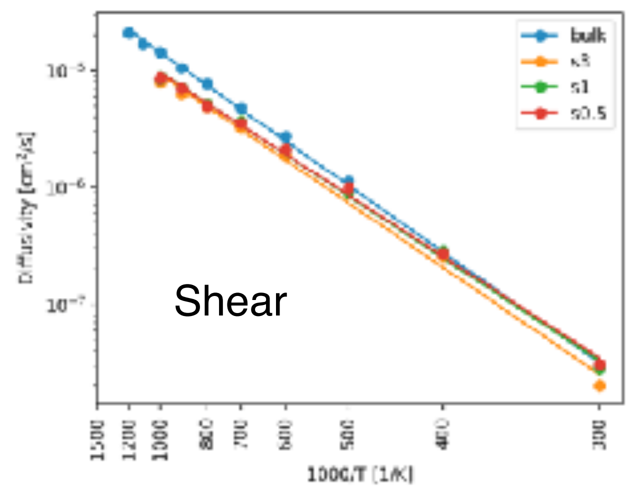
- Multiple mechanical deformation modes that may encounter in the composite is evaluated.
- Li+ diffusion has negligible decrease under small mechanical strain. More extensive deformation may induce slight more decrease in ionic conductivity.





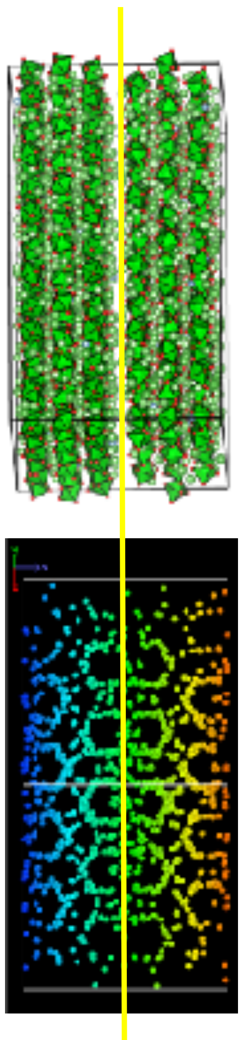






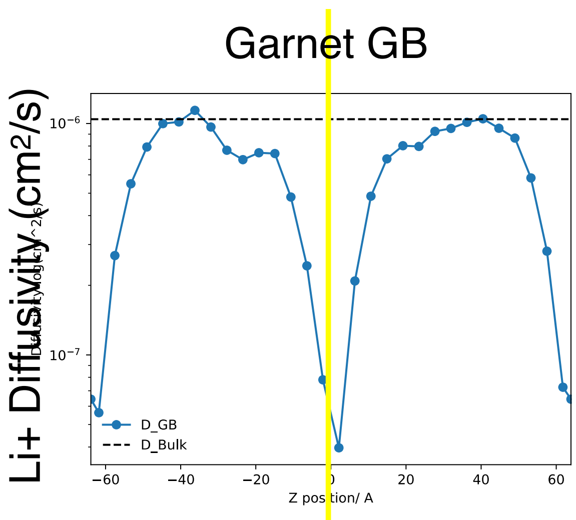
Grain Boundaries in Garnet : Effect on Diffusion and Dendrite Growth

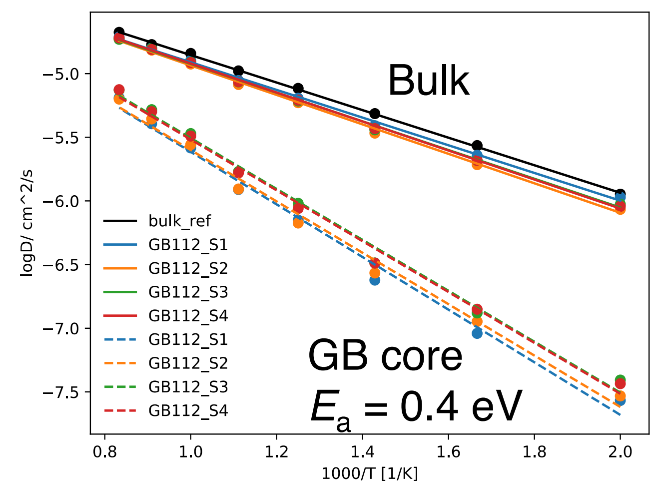
Garnet GB



In order to understand Li dendrite growth mechanism within garnet solid electrolyte, MD simulations were performed on garnet grain boundaries.

- Li+ diffusion decrease observed near GB core (~1nm).
- Slower down at garnet GB caused by distortion and disordering near GB core.
- GBs may cause significant potential drop or field concentration (may aid dendrite growth)



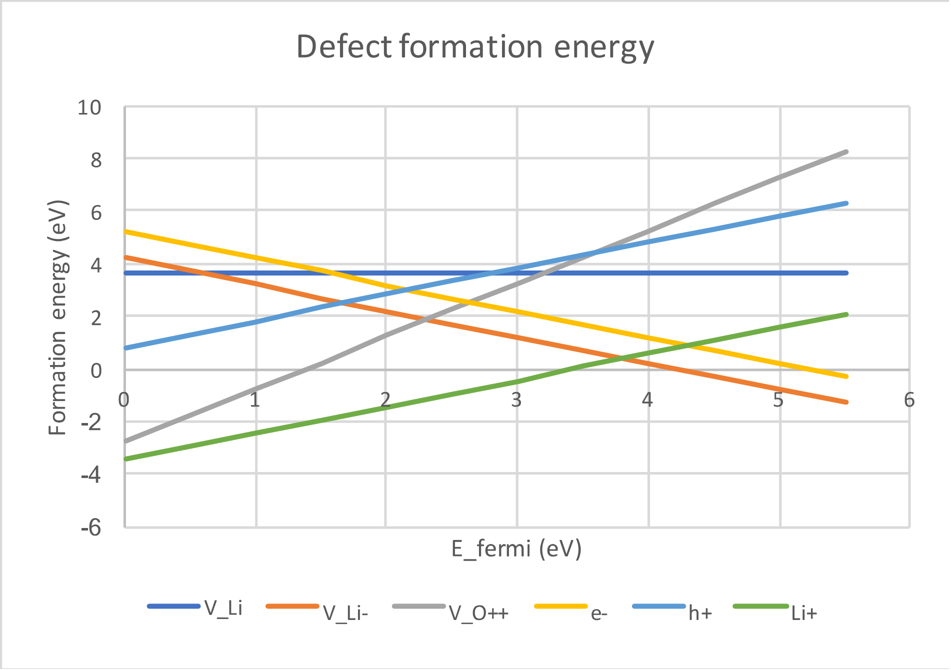


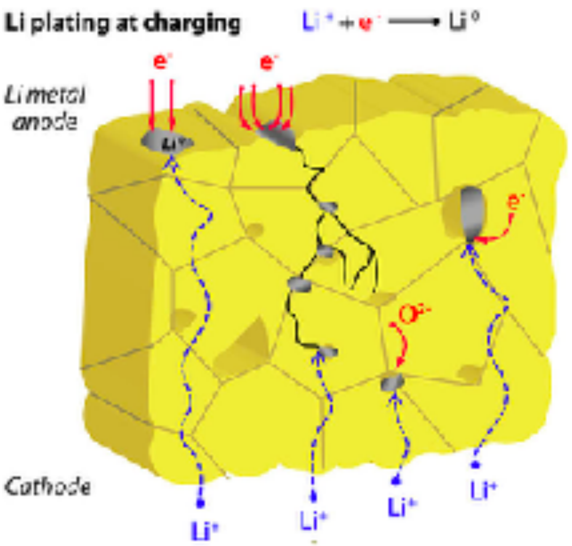
Defect Chemistry in Garnet and Effect on Li Dendrite Formation

The formation of other point defects in garnet may significant impact Li dendrite growth mechanism within garnet solid electrolyte.

First principles calculations were performed to evaluate various point defects in garnet.

- Li+ insertion into garnet may be favorable. (agree with ORNL TEM results. Ma, Chi et al. Nano letter 2016).
- Oxygen vacancy V_O may form at Li rich conditions (may aid Li metal reduction).
- e- polaron may also form (may aid dendrite formation).





Kilner et al ACS appl mater inter 2017

Response to Previous Year Comments

This project was not reviewed last year.

Collaboration and Coordination

Continued collaboration with Prof. Venkataraman Thangadurai
University of Calgary (co-inventor of garnet)

Remaining Challenges and Upcoming Work

- Achieving high current density Li cycling with thin (20 μm) hybrid electrolyte
- Demonstrating high energy density Li-S cells with the thin hybrid electrolyte

Proposed Future Research

FY18

- Fabricate < 20 μm electrolyte and determine Li/electrolyte interface up to 3 mA/cm^2

FY19

- Fabricate porous framework with mixed electron/ion conductivity
- Demonstrate Li-S cells with 450 Wh/kg

Any proposed future work is subject to change based on funding levels.

Summary

- Developed multiple approaches to make flexible hybrid polymer/garnet fiber electrolyte membranes:
  - Electrospun nanofibers
  - Templated fiber mats
- Fabricated flexible and scalable 4 cm X 4 cm garnet fiber mat
- Synthesized polymer garnet fiber hybrid electrolyte with good conductive properties
- Developing fundamental understanding of Li diffusion in garnet nanofibers and response to mechanical deformation
- Analyzed microstructures with FIB/SEM, AFM and profilometer
- Characterized electrochemical, mechanical and thermal properties of hybrid SSE.
- Fabricated hybrid SSE with a thickness of ~ 20 μm